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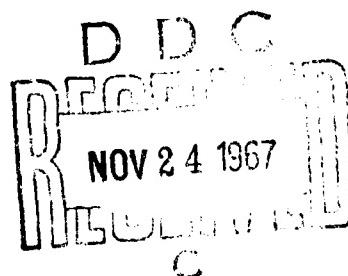


AIR FORCE CAMBRIDGE RESEARCH LABORATORIES

L. G. HANSCOM FIELD, BEDFORD, MASSACHUSETTS

The Conversion of Cubic to Hexagonal Silicon Carbide as a Function of Temperature and Pressure

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OFFICE OF AEROSPACE RESEARCH
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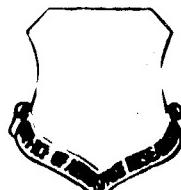
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This is a more complete version of the paper "Polytypism and the Beta-to-Alpha Transformation in Silicon Carbide," which was presented at the International Conference on Anisotropy of Single-Crystal Refractory Materials, held in Dayton, Ohio, on 13 to 15 June 1967.

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Abstract

Polytypism in silicon carbide is reviewed. The geometric properties of close-packed hexagonal structures are illustrated by models of the stacking arrangements in the more common polytypes. The inadequacies of a number of theories on the origin of polytypes are briefly discussed, and it is concluded that no satisfactory theory exists.

From the results of recent AFCRL experiments in the temperature range of 2100° to 2800°C, it is concluded that the transformation of beta to alpha silicon carbide can be suppressed by 20 atm of inert gas, and consequently that the alpha silicon carbide is a defect structure probably involving deficiencies in the carbon sublattice. It is further concluded that both polytypism and the beta-alpha transformation are impurity-dominated, and that the most significant impurities are boron and nitrogen. Speculating on the origin of polytypes, it appears that any adequate theory must include the influence of chemical and physical imperfections, temperature, and ambient gas composition and pressure.

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The Conversion of Cubic to Hexagonal Silicon Carbide as a Function of Temperature and Pressure

I. INTRODUCTION

Silicon carbide has unique chemical, physical, optical, thermal, and electrical properties that endow it with attractive possibilities as semiconductor material, particularly for difficult temperature and radiation environments and for electro-optical and high-power devices in normal environments. Despite substantial research efforts during the past two decades (O'Connor and Smilents, Eds., 1960; J. J. O'Connor, 1963; Knippenberg, 1963, pp. 181-274; Neuberger, 1965; Verma and Krishna, 1966), silicon carbide has failed to live up to its promise, primarily because certain problems associated with the controlled and reproducible growth of single crystals of this material have not been clearly understood.

In the silicon carbon system, the only compound species that exists in the solid state is silicon carbide, SiC (Elliott, 1966). It does, however, exist in both beta and alpha modifications. The beta, or cubic, modification crystallizes in the zinc-blende or sphalerite (diamond cubic) form. A large number (approximately 45) of the alpha are hexagonal or rhombohedral forms known as polytypes (Parthé, 1964).

At one time it was thought that the beta (cubic) modification was thermodynamically stable at low temperatures and that it transformed irreversibly to the alpha modification by a solid state phase transformation at about 2100°C (Jagodzinski and Arnold, 1960). Above this temperature the alpha modification was considered

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stable. It was also thought that the alpha polytypes were associated with slight energy differences involving different third-nearest-neighbor interactions in hexagonal close-packed structures. We now know that there has been no adequate explanation either for the beta-to-alpha transformation or for the origin of polytypes in silicon carbide.

It is the purpose of this paper to briefly outline the nature and present status of these problems and indicate the inadequacy of current theories. A number of experiments recently conducted at AFCRL are described. From the results of these experiments and our interpretation of experiments published by other workers, we draw some conclusions and speculate on the trend of current research.

2. POLYMORPHISM AND POLYTYPISM

When the same chemical compound exists in two or more crystallographic forms, the forms are called polymorphs and the phenomenon is called polymorphism. Polymorphs were originally associated with thermodynamic phases in such a way that the crystallographic form having the least Gibbs free energy was considered to be the most stable polymorph in a given range of temperature and pressure. To explain kinetic aspects such as speeds of transition from one polymorphic form to another and polymorphs that are metastable, energy-barrier theories depending largely on details of bonding structure were developed.

In certain close-packed structures like SiC, ZnS, and CdI₂, there is a special one-dimensional sort of polymorphism called polytypism. Polytypes are alike in the two dimensions of the close-packed planes, differing only in the stacking sequence in the dimension perpendicular to the close-packed planes. Since all polytypes of SiC have close-packed structures, all have the same density (3.17 gm/cm⁻³). Consequently, gross pressure effects cannot be considered to be the prime factor in polytype formation. Since polytypes differ geometrically only in third- and higher-nearest-neighbor spacing, all of them have very nearly the same energy. Nevertheless, temperature alone seems inadequate to explain the relative stability and occurrence of certain polytypes.

3. CLOSE-PACKED STRUCTURES AND NOMENCLATURE

In order to deal more precisely with polytypes in silicon carbide and be able to illustrate the more prevalent ones with models (Verma and Krishna, 1966, Chap. 4), we must first review close-packed structures and develop a consistent set of notations.

Figure 1 shows a single layer of close-packed spheres of constant radius.

Each sphere is surrounded by six spheres whose centers A form the vertices of a regular hexagon. Half of the interstices (voids) between spheres, which look like triangles pointing upward (Δ), are labeled B. The other half, like triangles pointing downward (∇), are labeled C. The hexagonal coordinates of the A, B, and C points projected into the plane of the paper are: A(0, 0); B($a/3$, $2a/3$); C($2a/3$, $a/3$).

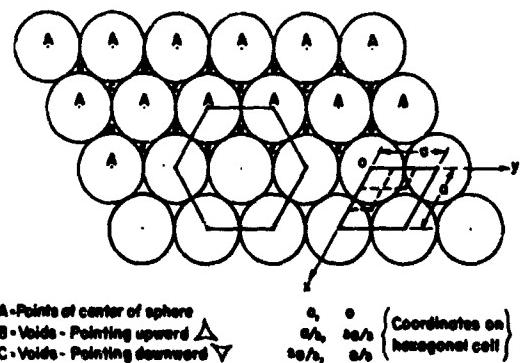


Figure 1. Single Layer of Close-packed Spheres of Constant Radius, With Positions of Centers of Spheres and Voids Projected Into Plane of Paper

If we pack a second layer over the first in a close-packed configuration, all the centers A' of the second-layer spheres will be directly above either the B or the C voids. Figure 2 shows the two possible arrangements of packing a second layer above the first. In Figure 2(a) the second-layer centers A' are above the B voids of the first layer; in 2(a') they are above the C voids. Each sphere of the second layer touches three spheres of the first layer; similarly, each sphere of the first layer

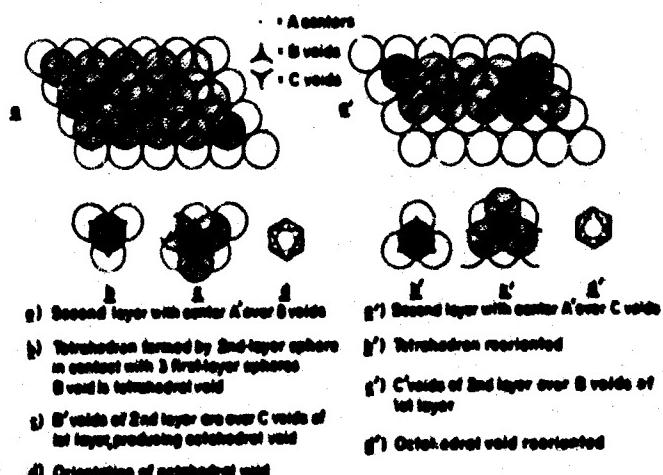


Figure 2. Two Layers of Close-packed Spheres of Constant Radius

touches three spheres of the second layer. The centers of the four spheres in contact form the vertices of a regular tetrahedron. By comparing 2(a) and 2(a') it can be seen that the tetrahedrons surrounding the C voids are both translated and rotated with respect to those surrounding the B voids. Looking into the voids of the second layer in Figure 2(a), we see half of them directly above the A points of the first layer and half directly above the C voids; the voids above the A points are tetrahedral whereas those above the C voids are octahedral. In Figure 2(a') the second-layer centers A' are directly above the C voids, the B' voids are directly above the A points, and the C' voids are directly above the B voids. Both position and orientation of the octahedral voids as well as of the tetrahedral voids therefore differ from Figures 2(a) to 2(a'). Thus, when a third layer is added (Figure 3) there are four possibilities of stacking: ABA, ACA, ABC, and ACB—that is, any sequence in which neither A nor B nor C succeeds itself. The ABA pattern leads to the hexagonal wurtzite structure, and the ABC pattern leads to the cubic zincblende structure. The ACA and ACB, the respective reverse stacking patterns for wurtzite and zincblende, are equivalent to the obverse patterns but often neglected.

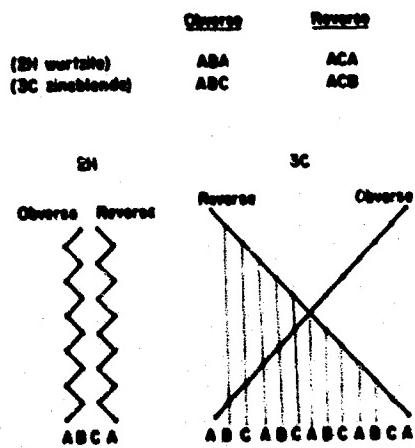


Figure 3. Three Layers of Close-packed Spheres of Constant Radius

Without stacking faults in the cubic structure, the sequence ABCABC would repeat indefinitely. If, however, during growth, any layer shifted position to present one set of voids rather than the other (Figure 2), the subsequent layers would follow the reverse pattern rather than the obverse, or, ABCABC... would become ABCABCACBACB with the fault in the position shown by the arrow. One such fault is equivalent to a twin fault in the cubic configuration (see Figure 4).

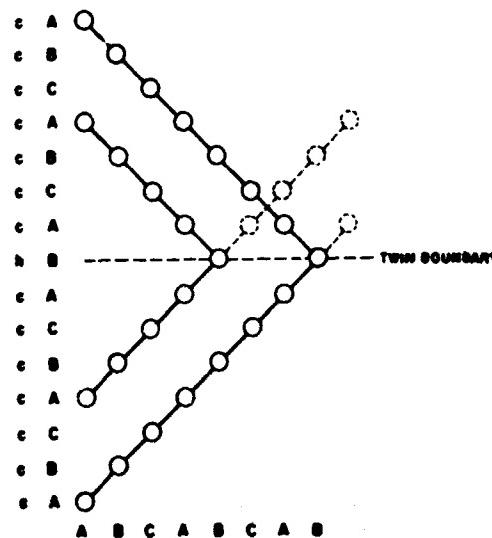


Figure 4. Twin Fault in Cubic Configuration

The polytypes we discuss here have the ABC sequences and standard nomenclature shown in Figure 5. The H, C, and R in the Ramsdell notation designate hexagonal, cubic, and rhombohedral respectively. The numeral represents the number of layers in the Z direction before the cycle repeats. In the Zhdanov notation, the first figure represents the number of transitions in the obverse direction, the second figure represents those in the reverse direction, and so on. The sum of the figures represents the number of layers in the period. Designations such as (23)₃

Ramsdell	Zhdanov	ABC Sequence	Hoppe	PW, *Ramsdell
2H	11	AB	--	(AB)
3C	00	ABC	++	ABC
4H	22	ABCBA	++--	ABCBA + (ABC)
5H	33	ABCACBA	++---	ABCACBA + (ABCAB)
6H	44	ABCACBACBA	++++--	ABCACBACBA + (ABCACB)
10H	(23) ₃	ABCACBACACACACBA	(++)--	(ABCACBACACACACBA)
12H	(34) ₃			
13H	(3323) ₃			
9H	(333332) ₃			
8H	(223, 3322) ₃			

*Pilling, Wyckoff, Jagendorf

Figure 5. Common Polytype Notations

are simply shorthand expressions for writing 232323, etc. The Hagg and Pauling-Wyckoff-Jagodzinski notations are slight variations of the Zhdanov scheme. A few of the higher polytypes have been included to indicate the complexity of some of the rarer polytypes and their structural relationships to the simpler ones.

Figure 6 is a photograph of a model of the 2H polytype, with the silicon and carbon atoms respectively represented by the large and small spheres. The next six figures (Figures 7 through 12) are sketched models of some of the more common polytypes, showing 3C, 2H, 4H, 6H, 8H, and 15R respectively. Figure 13 shows the ABC sequences of these polytypes plotted in the $1\bar{1}20$ plane. This type of diagram shows more clearly than the models that the 2H type reverses stacking sequence every layer; the 4H, after every two layers; the 6H, after every three layers; the 8H, after every four layers; and the 15R reverses alternately after first two and then three layers, and hence must go through three cycles to complete a period. The order of frequency of polytype occurrence is: 6H (by far the most common), 15R, 4H, and 8H; all others are quite rare.

So far, we have considered only the geometry of the problem and found polytypes to be ordered sets of C axis stacking faults, in which the faults are most likely to occur after every third layer and somewhat less frequently after two or four layers. Thus, the Zhdanov notation for the more common polytypes is dominated by 3, 2, and 4 sequences, in that order.



Figure 6. Model of 2H Polytype With Both Silicon and Carbon Atoms

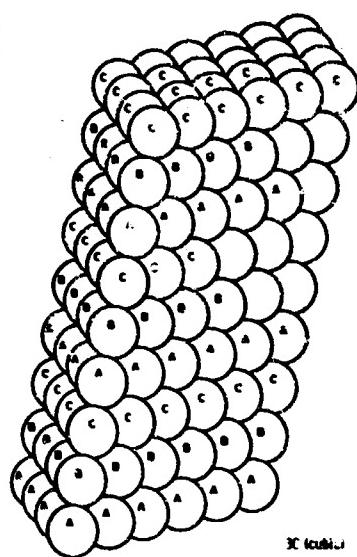


Figure 7

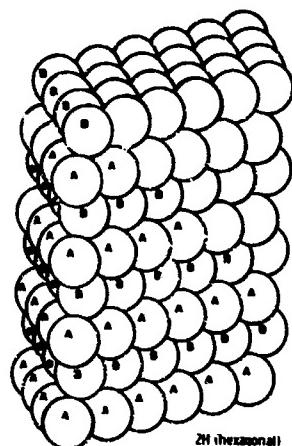


Figure 8

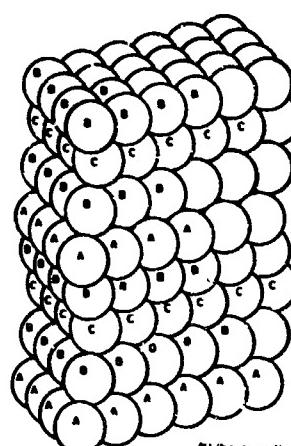


Figure 9

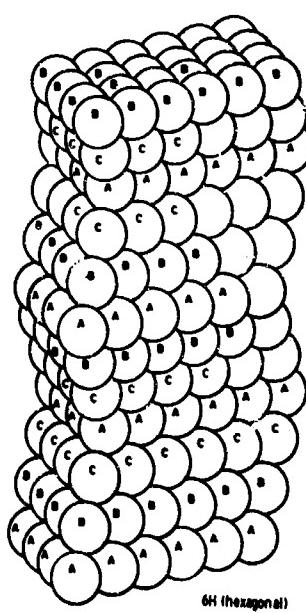


Figure 10

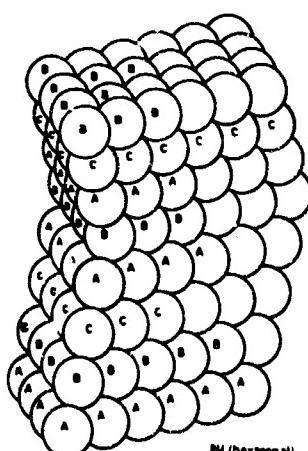


Figure 11

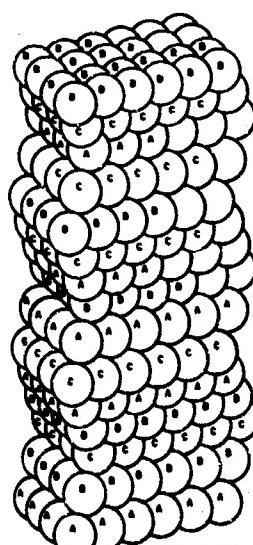


Figure 12

Figures 7-12. Model Configurations

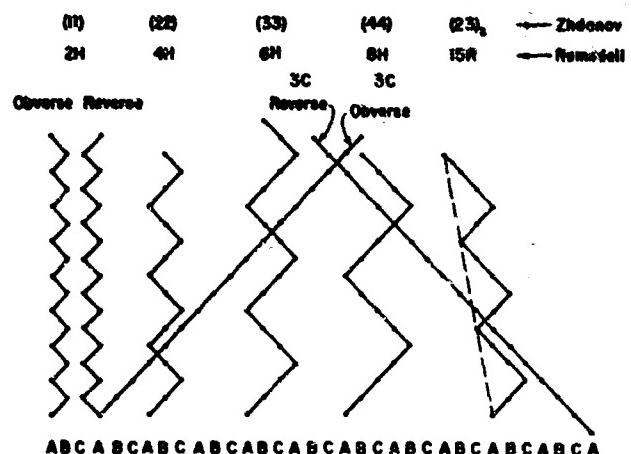


Figure 13. Position of Atoms in the $1\bar{1}\bar{2}0$ Plane

4. THEORIES ON THE ORIGIN OF POLYTYPES

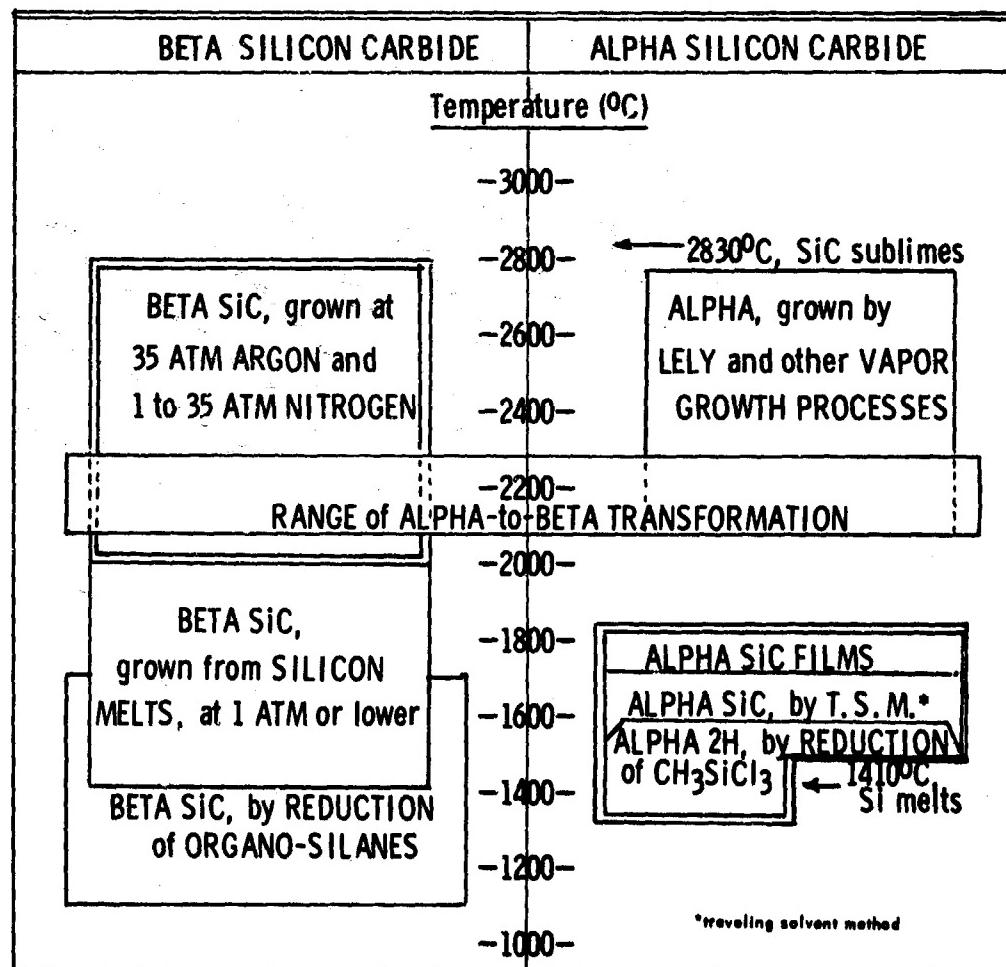
The real problem for the chemist and physicist is to explain why the stacking faults occur in orderly sequences leading to discrete polytypes with large precisely defined unit cells. In brief, the problem is to explain the origin of polytypes. There are almost as many theories as there are workers in the field, but they are generally based on considerations of temperature and energy, such as proposed by Jagodzinski; based on screw dislocations as the means of propagating polytypes, as proposed by Frank; or based on impurities, as proposed by Lundquist and others. These theories and others are explained in Verma and Krishna's book on polymorphism and polytypism in crystals (1966, Chap. 8).

We fail to see how energy theories can explain the relative stability and frequency of various polytypes. The screw dislocation theories may in certain cases explain the propagation of polytypes but hardly their origin. In general, SiC is prepared under experimental conditions that make it difficult to control its purity, and experimental evidence in support of current impurity theories is contradictory. Verma concludes that there is no satisfactory unified theory to explain the phenomenon of polytypism. A more complicated theory is apparently required—a theory that includes several variables rather than energy, imperfections, or chemical impurities alone. We will make some speculations about such a theory after the companion problem of the beta-to-alpha transformation is developed.

5. METHODS OF PREPARING SILICON CARBIDE

Figure 14 shows the various methods by which silicon carbide is usually prepared. First, neglecting the double-bordered blocks, it is seen that alpha silicon carbide, as

generally prepared from the vapor phase by the Lely process or some modification of it (Knippenberg, 1963, pp. 161-274; Hamilton, 1960), has been obtained in the temperature range from about 2300° to 2700°C. Beta silicon carbide, prepared either from silicon melts (Nelson, et al., 1966) in carbon crucibles, or by the hydrogen reduction of organo-silanes (Knippenberg, 1963, pp. 161-274; Jennings et al., 1966), has been obtained at temperatures well below 2000°C. Heat-treated in an inert atmosphere in the range 2100° to 2300°C, beta silicon carbide transformed to alpha silicon carbide (Knippenberg, 1963, p. 242). Hence, the simple conclusion that beta was the low-temperature modification and alpha the high-temperature modification.



*traveling solvent method

Figure 14. Temperature Ranges for Various Methods of Growing Alpha and Beta Silicon Carbide

Two papers at the Boston Conference on Silicon Carbide, sponsored by AFCRL in 1959, confused this simple picture. Merz and Adamsky (1960, 1959) reported the growth of the 2H modification (wurtzite) for the first time. Their 2H (alpha) crystals were small whiskers intergrown with beta silicon carbide prepared by the hydrogen reduction of methyltrichlorosilane (CH_3SiCl_3) in the temperature range 1300° to 1600°C. They concluded that this finding required reevaluation of the theory that it was beta that was the low-temperature form of silicon carbide. Scace and Slack (1959, 1960) reported that the silicon carbide obtained in the course of their solubility studies was beta even at preparation temperatures above 2600°C. Thus, in these cases the alpha form was prepared at low temperatures and the beta at high temperatures.

Figure 14 shows that factors other than temperature determine the form, whether cubic or hexagonal, that will be attained. Experiments conducted at AFCRL (Ryan et al., 1966), reported at the International Conference on Crystal Growth in June 1966, verified Merz and Adamsky's results in preparing 2H SiC whiskers. Further, they extended those results by demonstrating that the growth of the 2H crystals was obtained by means of the vapor-liquid-solid method, hence dominated by impurities, and that through an appropriate choice of impurities, 2H (beta) whiskers could be grown at will. The low-temperature growth of alpha SiC was thus adequately explained.

Both in our laboratory and through contractors (Nelson et al., 1967), we have conducted extensive investigations of beta silicon carbide grown from silicon melts. Practical limitations of this process have encouraged us to consider the possibilities of suppressing the beta-to-alpha transformation and to reevaluate the possibility of growing beta crystals in the higher temperature region. This is the subject of our present investigations.

Figure 15, taken from Elliott's (1966) First Supplement to Hansen's Constitution of Binary Alloys, compares silicon carbide phase diagrams from two sources. The large difference between the two is some indication of the difficulty of making measurements of this type at high temperatures. If the solid curve were not unfortunately incorrect, the problem of growing beta silicon carbide from solution would be relatively easy.

The broken curve in Figure 15 is based on Scace and Slack's data (1959, 1960), which they replotted in terms of solubility in the figure we show as Figure 16. Now we can clearly see the problem of growing SiC from silicon solution at 1 atm. If we attempt growth below 2000°K (~1700°C), which is 0.5 on the $10^3/T, ^\circ\text{K}$ scale, the solubility is less than 0.1 atomic percent. Low solubility and high supersaturation leads to uncontrolled nucleation and limits the size of the crystals. If we increase the solubility by increasing the temperature or by introducing additives in the melt, the crystals have alpha inclusions.

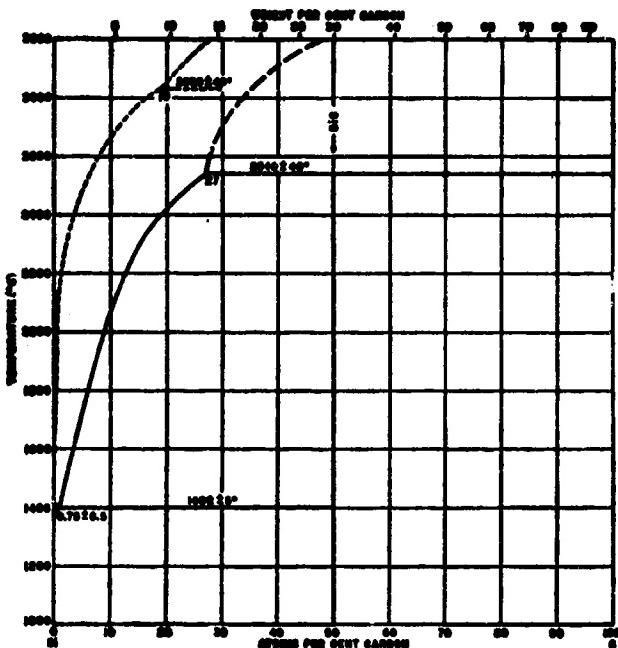


Figure 15. Silicon Carbon Phase Diagrams (from Elliott, 1966; --- Scace and Slack, 1959; — Doloff, 1959)

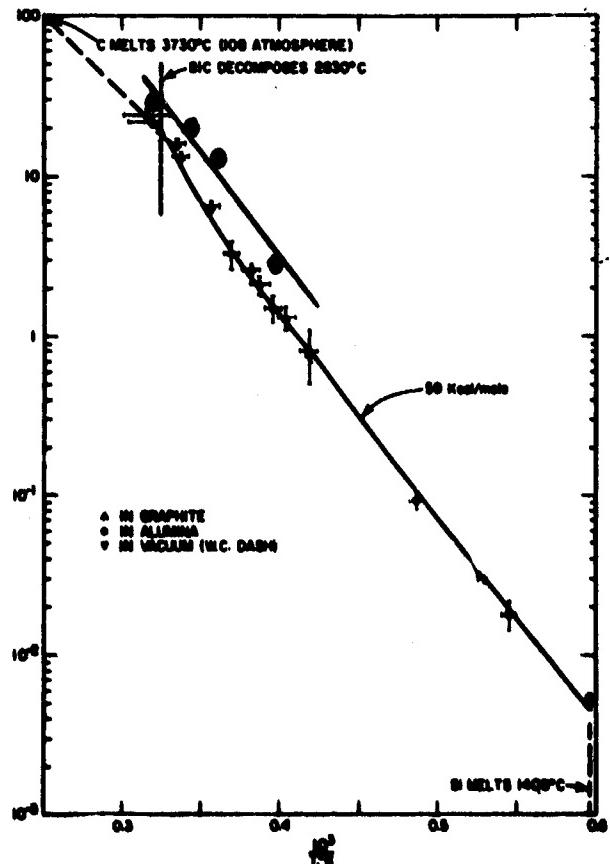


Figure 16. Solubility (Atomic Percent) of Carbon in Liquid Silicon as a Function of Reciprocal Temperature (from Scace and Slack, 1960)

6. EXPERIMENTS

Experiments were conducted in a modified A. D. Little type-MP furnace that was driven by a 50-kW Lepel rf dual-frequency generator, monitored by a Leeds-Northrup automatic optical pyrometer, and capable of operation from 10^{-5} Torr to 20 atm (Figure 17). A cutaway view of the furnace arranged for Czochralski growth is shown in Figure 18. Details of the test chamber as used in the experiments reported here are shown in Figures 19 to 21.

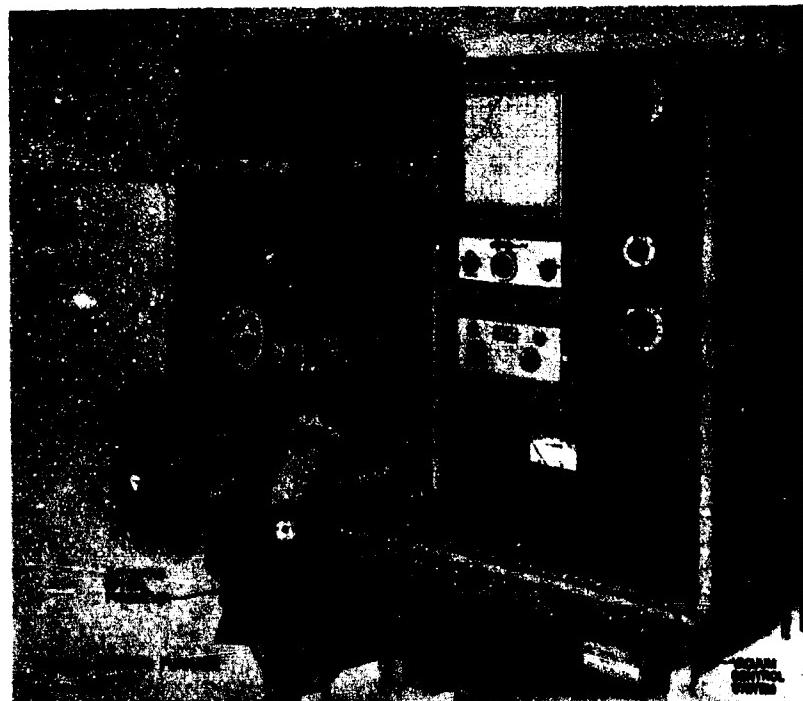


Figure 17. Modified MP Furnace for High-temperature Experiments



Figure 18. Cutaway View of Furnace

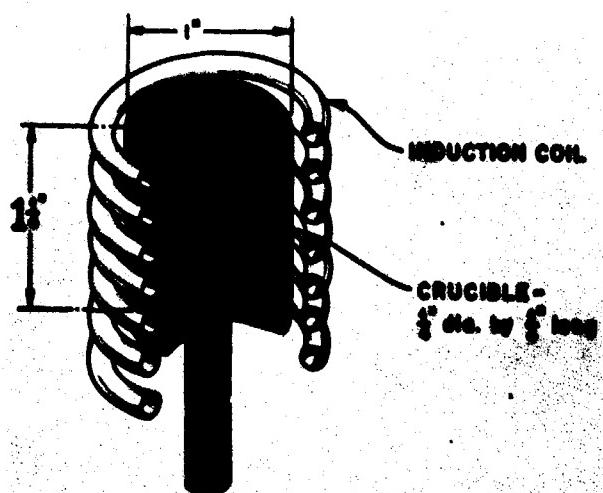


Figure 19. Susceptor and Crucible Arrangement



Figure 20. Disassembled View of Susceptor and Crucible

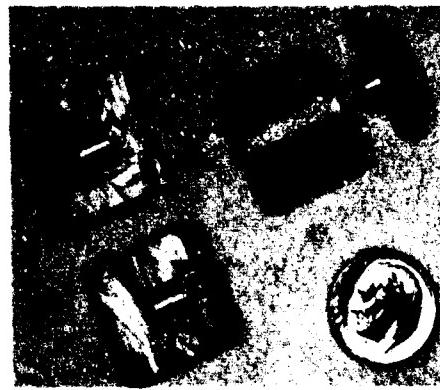


Figure 21. Disassembled View of Crucible

A typical calibration curve is shown in Figure 22. The pyrometer was sighted in to the crucible chamber through a small hole drilled through the top of the crucible. The crucible chamber radiated like a black body. The pyrometer readings plotted against the induction-heater plate current were easily reproducible to $\pm 20^\circ\text{C}$. An

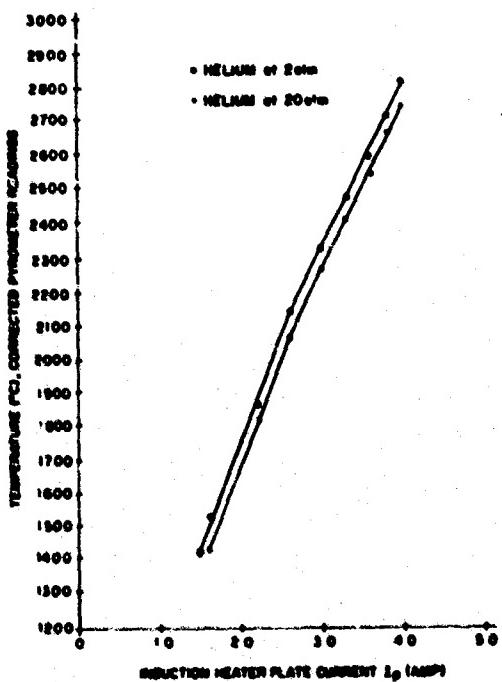


Figure 22. Calibration of MP Furnace in Helium Atmosphere

independent check on this relative calibration was made with materials of known melting points. High-temperature reactions and eutectics that formed with the carbon of the crucible presented problems. Among the materials successfully used were sapphire (mp 2050°C) and a specially prepared sintered molybdenum carbide (mp 2695°C). The melting points were in excellent agreement with the calibration curves. We judge our readings to be good to $\pm 30^\circ\text{C}$ and at least better than $\pm 50^\circ\text{C}$.

The carbon susceptors were outgassed for several hours at about 2500°C and 10^{-5} Torr, after which they were mass spectrographically pure. The crucible charge was silicon in which the impurities averaged no more than 1 part/10⁹.

The solubility points plotted in Figure 16 correspond to 2250°, 2450°, 2650°, and 2850°C. Although our own three sets of measurements are in good agreement with each other, isothermal conditions did not exist in the test chamber and we consider our apparent solubility values to be substantially too high. Hence, we are quite confident that the Scaife and Slack phase diagram (in Figure 15) is much nearer correct than Doloff's, which shows even higher solubility than ours.

Table 1 lists the data on 16 experiments in which we used pure silicon as the crucible charge. The first 11 experiments provided the solubility data. More

Table 1. Summary of 16 Experiments With Pure Silicon Charge in Crucible

Exper. No.	Temp. (°C)	Time (min)	Gas	Press. (atm)	Beta only	Beta and trace α	Alpha and trace β	Alpha only	Solubility (atomic %)
72	2850	2	argon	20		x			30
94A	2850	5	argon	20		x			31
74D	2650	10	argon	20		x			22
85A	2650	5	argon	20		x			19
94B	2650	5	argon	20	x				18
74C	2450	10	argon	20		x			10
85B	2450	5	argon	20		x			-
94C	2450	5	argon	20	x				15
74B	2250	10	argon	20		x			3.2
85C	2250	5	argon	20		x			2.2
94D	2250	5	argon	20	x				-
79	2450	60	helium	20		x			
90	2450	60	argon	20	x				
98B	2450	3	helium	2			x		
97	2250	3	argon	20	x				
98A	2250	3	argon	2		x			

important, however, they showed that even at 2850°C the silicon carbide yield is primarily beta silicon carbide and that the beta-to-alpha transformation is suppressed at 20 atm of argon.

Runs 79 and 80 showed that the beta form is not due to the short time-temperature cycles used in the solubility runs. Runs 79 and 98B showed that the beta-to-alpha transformation is suppressed by 20-atm pressure, the pressure that was used to prevent dissociation of SiC by evaporation of silicon. This finding is important because it indicates that the transformation is associated with physical or chemical defects in the alpha structure and that it can be prevented by practical procedures such as the application of small excess pressures of inert gas.

Addiamano and Staikoff (1965) have succeeded in suppressing beta-to-alpha conversion up to 2500°C by using 1 atm of nitrogen, or 1 atm of argon that includes at least 400 Torr of nitrogen. They found that the beta-to-alpha transformation was irreversible in the nitrogen atmospheres used (apparently to about 1 atm).

Slack and Scace (1965) have reported the formation of beta silicon carbide from 6H alpha material in 30 atm of nitrogen at a temperature of about 2450°C. They implied that this was a vapor phase conversion.

Quite recently, Kieffer Gugel, Ettmayer, and Schmidt (1966) have reported that silicon carbide can be converted from beta to alpha reversibly and repeatedly. They converted alpha to beta by treatment for 30 min at 2500°C in nitrogen at from 2 to 30 atm pressure and then converted the beta to alpha by reheating the material for 30 min at 2500°C in 1 atm of argon. Since these experiments were carried out with polycrystalline microgranular silicon carbide, it is not clear whether or not the direct and/or reverse transformation was via the vapor state.

In a series of experiments with argon, helium, and nitrogen atmospheres in the temperature range from 2200° to 2800°C, we used the same type of crucible as in our solubility experiments. As the charge, however, instead of pure silicon we used beta silicon carbide. This material was made by the silicon melt process at about 1530°C under conditions of extreme purity in the furnace already described. It showed no trace of alpha inclusions on x-ray measurements, and only very small traces of impurities by mass spectrographic and neutron activation analyses. Seventeen of these experiments are summarized in Table 2.

Runs 95 and 96 show unambiguously that it was the excess pressure rather than the excess silicon that suppressed the beta-alpha transformation. In runs 78, 87, 88, 89, and 91, helium was used as the inert gas. Helium acts essentially like argon, but it seems that there may be more impurities in the helium, leading to more alpha inclusions in the SiC. A comparison of the effect of nitrogen with that of helium strongly indicates that nitrogen suppresses the beta-alpha transformation not because of atom size alone but because it enters substitutionally into the carbon sublattice.

Table 2. Summary of 17 Experiments With Beta Silicon Carbide Charge in Crucible

Exper. No.	Temp. (°C)	Time (min)	Gas	Press. (atm)	Beta only	Beta and trace α	Alpha and trace β	Alpha only	Notes
71	2850	60	argon	20		decomposed			
75	2550	120	argon	20		x			
96	2550	30	argon	20		x			
95	2550	30	argon	2			x		
76	2450	60	argon	20		x			
77	2250	60	argon	20		x			
87	2550	30	helium	20		xx			(1)
88	2550	30	helium	2		xx	x		
89	2350	30	helium	20		xx	x		
91	2350	30	helium	2		xx	x		
78	2250	60	helium	20		xx			
92	2550	30	nitrogen	20	x, sand			x, SC	(2)
93	2550	30	nitrogen	2	x, sand			x, SC	(2)
100	2550	30	nitrogen	20				x	(3)
101	2400	30	nitrogen	20	x				(4)
103	2400	30	nitrogen	20	x, sand x, SC				(4)
102	2400	30	argon	2			x		(4)

Notes: (1) xx = beta with larger trace α

(2) alpha single crystal (SC) inserted into beta sand

(3) alpha single crystal (SC) inserted into alpha grains

(4) beta single crystal (SC) inserted into beta sand

Anomalies of nitrogen in SiC have been noted or studied by many people, including Hamilton (1960), Carroll (1960), Kroko (1966), Griffiths (1966), Slack and Seace (1965), Addiamano (1966), Knippenberg (1963, pp 161-274, and Kieffer et al. (1966), but no clear picture has emerged. Many people have speculated that nitrogen, which is a donor impurity, tends to stabilize the beta form, whereas boron, which is an acceptor, tends to stabilize the alpha. Such speculations are intuitively unsatisfying because they do not give a chemical or physical picture of the role of either the nitrogen or the boron. Since the doping level will rarely exceed 10^{19} atoms cm^{-3} , the conduction electron-to-atom ratio seems too small to influence the polytype structure. In Runs 92 and 93, a single alpha crystal was implanted in the granular beta charge. The single crystals were recovered after the run. The granular sand remained beta and the single crystals remained alpha, indicating that the reverse transformation from alpha to beta probably takes place only through the vapor state. In Run 101,

102, and 103, beta crystals were inserted into beta sand in the crucible. The results indicate that the direct transformation from beta to alpha probably takes place by a diffusion process, as suggested by Knippenberg (1963, pp 161-274), as well as via the vapor state.

7. CONCLUSIONS

The clearer picture emerging from these experiments is roughly illustrated in Figure 23. A relatively small excess pressure favors the growth of beta silicon carbide at all temperatures. This indicates that the alpha material is a defect structure. We speculate that the alpha is deficient in the carbon sublattice. It may be that at temperatures somewhat below those at which silicon evaporates, nitrogen outdiffuses from the carbon sublattice and leaves excess vacancies in it. Then boron, which normally substitutes for silicon in cubic silicon carbide (Gorin and Pletyushkin, 1964), may migrate to the carbon sublattice (Woodbury and Ludwig, 1961), introducing strain and precipitation of boron, which acts as the nucleus for the generation of screw dislocations, which in turn determine the polytype. Impurities, defects, temperatures, and ambient gas would in such a picture all influence toward polytypism.

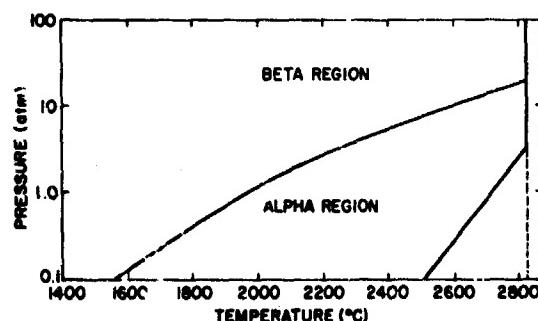


Figure 23. Estimated Temperature-Pressure Ranges for Formation of Alpha and Beta Silicon Carbide

We are quite confident that beta silicon carbide is the more perfect form; and that all the alpha modifications are associated with chemical and physical defects. Nitrogen and boron seem to be the principal impurities whose presence or absence not only enhances or inhibits the transformation from beta to alpha silicon carbide, but determines the particular polytype. Our investigations to clarify some of these points are continuing.

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13. ABSTRACT Polytypism in silicon carbide is reviewed. The geometric properties of close-packed hexagonal structures are illustrated by models of the stacking arrangements in the more common polytypes. The inadequacies of a number of theories on the origin of polytypes are briefly discussed, and it is concluded that no satisfactory theory exists. From the results of recent AFCRL experiments in the temperature range of 2100° to 2800°C, it is concluded that the transformation of beta to alpha silicon carbide can be suppressed by 20 atm of inert gas, and consequently that the alpha silicon carbide is a defect structure probably involving deficiencies in the carbon sublattice. It is further concluded that both polytypism and the beta-alpha transformation are impurity-dominated and that the most significant impurities are boron and nitrogen. Speculating on the origin of polytypes, it appears that any adequate theory must include the influence of chemical and physical imperfections, temperature, and ambient gas composition and pressure.		

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